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PATENT SPECIFICATION



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PROVISIONAL SPECIFICATION.

No. 6479, A.D. 1922.

Improvements in the Purification of Oils.

We, HARRY MACKENZIE RIDGE, of 2, Great Winchester Street, London, E.C., 2, and WILLIAM RICHARD HODGKINSON, of 89, Shooter's Hill, 5 London, S.E. 3, both British subjects, do hereby declare the nature of this invention to be as follows:—

This invention relates to an improved process for removing colour or odour or 10 both arising from the presence of sulphur compounds or undesirable unsaturated hydrocarbons or both or like impurities in oils, more particularly oils of mineral origin.

According to the invention a material of a porous nature is used partly on account of its physical nature and chemical composition and partly as a 15 means or medium for holding in a conveniently finely divided state an active or activating material. The oil is filtered through or otherwise brought into contact with the porous material.

A suitably porous and at the same 20 time absorptive or adsorptive material is dehydrated or partially dehydrated bauxite, and copper or an oxide of copper in a suitable activating material. The bauxite in suitably coarse powder or 25 granules may be impregnated with a solution of acetate of copper, or any organic salt of copper that can be destroyed by heating so as to leave either copper oxides or metallic copper or both, 30 or with an ammoniacal solution of copper such as cuprammonia. Preferably, the impregnation should introduce at least 1 per cent. of copper and generally more, into the carrying material. After 35 impregnation the material is heated in such manner that the copper compound is decomposed leaving copper oxide, copper suboxide or metallic copper or any two or more of these mixed, united 40

or disseminated in and on the bauxite or like material. 45

Copper oxide or copper suboxide or metallic copper in fine powder may be mixed by any mechanical means with the bauxite, but this method does not yield the intimate association afforded by impregnation. 50

Other materials than bauxite may be used as a base for holding the copper, for instance manganese oxide in moderately coarse powder, some magnesium minerals (carbonate, silicate), iron oxide or iron silicate, coarse copper oxide prepared from wire or shot copper, granulated copper, etc. These materials, 55 after use as a purifying material, are recoverable by draining or otherwise separating part or all of the adherent oil and then heating or otherwise treating in such manner that any organic matter or carbon is removed and the copper material reoxidised. 60

After this it is advisable to moisten with water or slake whilst hot or to pass steam over the hot material until it cools to a convenient temperature for re-introduction into the apparatus or purifying vessel, providing that the temperature be sufficiently high to avoid the presence of actual water or moisture. 65

The temperature of this reheating should not be high enough to interfere with any water which may be combined in the materials as water of hydration. 70

When the activating material is copper oxide, copper suboxide, metallic copper or a mixture of any two or more of these, it may be used alone. 80

Dated this 4th day of March, 1922.

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[Price 1/-]

PROVISIONAL SPECIFICATION.

No. 14,424, A.D. 1922.

Improved Process of Purifying Oils and the like.

We, HARRY MACKENZIE RIDGE, a British subject, of 2, Great Winchester Street, London, E.C. 2, and WILLIAM RICHARD HODGKINSON, a British subject, of 89, Shooter's Hill Road, London, S.E. 3, do hereby declare the nature of this invention to be as follows:—

This invention relates to a process of purifying oils. The oil is treated with metallic copper, preferably in a state of more or less fine powder or grains containing also a certain amount of one or both of the oxides of copper.

A suitable material may be made either by starting with moderately finely divided copper metal such as turnings or filings or the like and partially superficially oxidising this, or by starting with a granular oxide of copper (CuO) and partially reducing this by gently heating it in a closed or partly closed vessel with an insufficient quantity of some organic reducing agent such as a clean oil, alcohol, sugar or the ammonia salt of any kind of organic acid, or of hydrogen gas or carbon monoxide or some other known reducing agent in a clean condition; the product in the latter case is a mixture of oxide of copper (CuO) as the basis on which is a layer more or less thin of cuprous oxide (Cu_2O) and metallic copper. The metal being finely divided, sometimes crystalline, is attached to the basis of oxide.

This material is used either as a

direct filtering medium or for agitation with the oil in a suitable vessel. After this treatment, which tends to remove sulphur compounds in the first place, the oil may be filtered through or otherwise treated with bauxite or any other of the materials usually used for the purpose in the ordinary way. As another method there may be added to the metallic copper and the oxides of copper a small amount, say 5 per cent. of one of the sub-halides of copper, for instance, and by preference, the sub-chloride Cu_2Cl_2 , may be incorporated therewith whereby the treatment with bauxite, above mentioned, may be avoided.

The sub-chloride of copper may be prepared in any known manner and added to the mixture of copper and its oxides, or it may be formed by using salammoniac as the reducing agent for the copper oxide, whereby a small suitable amount of Cu_2Cl_2 is formed and disseminated through the mass of the material.

Preferably, a suitable amount of an organic reducing agent should be used together with the sal-ammoniac to ensure the presence of sufficient metallic copper.

The material can be regenerated by any suitable method.

Dated this 22nd day of May, 1922.

ABEL & IMRAY,
Agents for the Applicants.

PROVISIONAL SPECIFICATION.

No. 14,425, A.D. 1922.

Improved Process of Purifying Oils and Materials therefor.

We, HARRY MACKENZIE RIDGE, a British subject, of 2, Great Winchester Street, London, E.C. 2, and WILLIAM RICHARD HODGKINSON, a British subject, of 89, Shooter's Hill Road, London, S.E. 3, do hereby declare the nature of this invention to be as follows:—

This invention relates to a treatment of oils and the like to remove impurities such as sulphur compounds, unsaturated compounds of carbon and hydrogen and other similar compounds which may have an unpleasant odour or other undesirable properties, and to a material therefor. The material is metallic copper, in a granular or more or less finely divided state so that the coarser

pieces or particles thereof are coated by or mixed with finely divided copper such as is produced by the reduction of an oxide or other compound of the metal to the metallic state by means of some reducing agent as a hydrocarbon, hydrogen, ammonia compound of an organic acid or salammoniac or other like agent, the reduction preferably occurring at the lowest practicable temperature and without melting, the said copper being mixed with or containing adhering to it a small amount, say 5-10 per cent. of the sub-chloride of copper Cu_2Cl_2 , sub-bromide or iodide. We prefer that the mixture should contain copper in the metallic state and the sub-chloride only, but a

proportion (like 20 per cent.) of the oxides of copper Cu_2O and CuO may also be present but so that the main bulk of the mixture be the metal. The oil to be treated is either agitated with or filtered through the cupriferous material for such time or at such rate as is essential for the purpose.

After use the material may be

recovered and used again with little or no impairment or loss and where sulphur has been removed from a substance the sulphur may be recovered by some known method.

Dated this 22nd day of May, 1922.

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ABEL & IMRAY,
Agents for the Applicants.

PROVISIONAL SPECIFICATION.

No. 17,585, A.D. 1922.

Improved Process for Purifying Oils or the like.

We, HARRY MACKENZIE RIDGE, a British subject, of 2, Great Winchester Street, London, E.C. 2, and WILLIAM RICHARD HODGKINSON, a British subject, of 89, Shooter's Hill Road, London, S.E. 3, do hereby declare the nature of this invention to be as follows:

25 This invention relates to a process of purifying oils or the like, more particularly for removing sulphur therefrom. The oil in the form of liquid or vapour is brought into intimate contact with material consisting of or carrying one or both of the metals zinc or cadmium, or of oxides or salts of these metals, or, less efficiently, consisting of or carry-

ing iron or an oxide or a salt thereof.

The material is more active if it contain or consist of a mixture of the metal and its oxide. The amount of oxide mixed with the metal need not be large, indeed in most cases the amount of oxide which is produced and carried on the surface of the metal, by oxidation, suffices.

The material acts more rapidly if it is previously dried so as to remove adherent or adsorbed water.

Dated this 26th day of June, 1922.

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ABEL & IMRAY,
Agents for the Applicants.

COMPLETE SPECIFICATION.

Improved Process for Purifying Oils and the like.

We, HARRY MACKENZIE RIDGE, a British subject, of 2, Great Winchester Street, London, E.C. 2, and WILLIAM RICHARD HODGKINSON, a British subject, of 89, Shooter's Hill Road, London, S.E. 3, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:

60 The purification of oils by means of metals, metal oxides or metal salts, including chlorides, particularly such as by their affinity for sulphur tend to remove this constituent and also sulphur compounds, has been recommended by many inventors. Nevertheless, such a purification is not practised.

In investigating this mode of purification we have found that of the many metals which have been prescribed, copper, zinc, cadmium and iron are active for the purpose, but this activity is practically absent in the absence of an oxide of the metal. For instance copper free from the film of copper oxide which is normal to the commercial metal has but little value in the direction in question. This discovery led to

the use of mixtures of the metals in question with their oxides; greatly improved results were obtained and it was further found that a chloride of the metal could be used instead of a part or the whole of the oxide.

According to this invention, the oil, particularly mineral oil, in the form of liquid or vapour is brought into intimate contact with material consisting of or carrying one or more of the metals copper, zinc, cadmium or iron, together with one or more oxides or halides or oxyhalides of these metals. Particularly to be recommended is a mixture of copper with an oxide of copper or a halide or oxyhalide, especially the subchloride of copper.

The proportion of oxide or halide need not be large.

A good material for the purpose may be made, when this is practicable, as in the case of copper oxide, by more or less superficially reducing the oxide.

The material acts more quickly if it is previously dried so as to remove adherent or adsorbent moisture.

The material may be used as a direct filtering medium for the liquid oil, in

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which case it must be in suitable condition as to its state of subdivision or porosity, as will be well understood. Or the material in a more or less finely subdivided state may be agitated with the liquid oil in a suitable vessel.

When the vapour is to be treated, it may be passed through a column or layer of the material in suitable state of subdivision. Alternatively the material may be placed between two vertical perforated plates or wire gauze and the vapour passed through the layer of material.

15 The following examples illustrate the invention:—

EXAMPLE 1.

Copper turnings or filings are heated for a few minutes with full access of air, so that they become partially coated with CuO or Cu₂O or both. Before it has had an opportunity of acquiring superficial moisture from the atmosphere, the copper is charged into a drum containing the oil to be treated and adapted to be agitated. The proportion of copper to oil depends on the nature of the latter; in the case of a shale oil high in sulphur the partially oxidised copper may conveniently be 12 per cent. of the weight of the oil. The proportion is, however, easily determined by a small scale experiment, and if excess of the copper be used, it may serve for the treatment of a further charge of oil. The content of the vessel is agitated until a test portion of the oil shows the desired degree of purification as indicated by its colour, sulphur content or other test. The oil is then discharged from the drum and filtered, if necessary.

EXAMPLE 2.

Granulated copper oxide is gently heated in a closed or partly closed vessel with any suitable reducing agent free from sulphur, the proportion being, say 10 per cent. of that necessary to reduce the oxide to metal. The product is a mixture of CuO as the basis, on which is a layer more or less thin of Cu₂O and copper. This material is used in the manner described in Example 1.

EXAMPLE 3:

55 Granulated copper oxide is gently heated with about 10 per cent. of its weight of sal-ammoniac and 5 per cent. of its weight of a paraffin lubricating oil. The product is a mixture of oxides of copper, metallic copper and cuprous chloride. It is used while still hot for packing a filtering vessel, through which the oil to be purified is passed as often as

may be necessary to produce the required degree of purification.

EXAMPLE 4.

65 Granulated copper oxide is completely reduced at the lowest practical temperature and is mixed in a revolving drum with 5—10 per cent. of its weight of cuprous chloride made in any known manner. The mixture is dried at a temperature about 100° C. and used as described in Example 3.

70 Means are known for obtaining the materials used according to this invention in a state distributed over the surface of such material as pumice, bauxite and the like, and may be applied for obtaining materials suitable for purifying oils in accordance with this 80 invention.

75 For example, dehydrated or partially dehydrated bauxite in suitably coarse powders or granules is impregnated with a solution of acetate of copper of, say, 85 10 per cent. strength and is then heated to leave a mixture of copper and its oxides in the bauxite.

80 It is not essential that the bauxite, pumice or the like should carry the metal oxide or salt or mixture of these in the sense that it has been impregnated; where it is desirable it may merely contain the metal and oxide or halide or mixture of these, being prepared by a 95 simple mixing operation.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we 100 claim is:—

1. A process of purifying oils or the like, particularly of removing sulphur therefrom, which consists in bringing the oil in the form of liquid or vapour 105 into intimate contact with a material consisting of, carrying or containing both one or more of the metals copper, zinc, cadmium or iron and an oxide or a halide, or both, of the metal or metals. 110

2. A process as referred to in Claim 1, wherein the material consists of, carries or contains both copper and cuprous chloride or other halide or oxyhalide.

3. A process as referred to in Claim 1, 115 wherein the material is made by partially reducing copper oxide.

4. A process as referred to in Claims 1 and 2, wherein the material is made by partially reducing and partially 120 chlorinating copper oxide.

Dated this 4th day of September, 1922.

ABEL & IMRAY,
Agents for the Applicants.